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14. ABSTRACT

Several bromide salts composed of methylimidazolium cations possessing unsaturated sidechains (allyl-, 3-butenyl-, propargyl-, 2-butynyl-, and 2-pentynyl-) have been synthesized and characterized by multinuclear NMR, vibrational spectroscopy, and DSC, X-ray and elemental analysis. X-ray structures of 1-(2-butynyl)-3-methylimidazolium bromide, 1-propargyl-3-methylimidazolium bromide as well as the X-ray structure of 1-allyl-3- methylimidazolium bromide which was previously identified as a room temperature ionic liquid, were all determined.

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Alkene- and Alkyne-substituted Methylimidazolium Bromides: Structural Effects and Physical Properties

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Abstract. Several bromide salts composed of methylimidazolium cations possessing unsaturated sidechains (allyl-, 3-butenyl-, propargyl-, 2-butynyl-, and 2-pentynyl-) have been synthesized and characterized by multinuclear NMR, vibrational spectroscopy, DSC, and elemental analysis. Crystal structures of 1-(2-butynyl)-3-methylimidazolium bromide, 1-propargyl-3-methylimidazolium bromide and 1-allyl-3-methylimidazolium bromide, were determined.

Keywords: Ionic liquids; Methylimidazolium; Bromides; DSC; Crystal structure

Introduction

In recent years, ionic liquids have become a material class of intensive research and development [1−7]. They owe their popularity to the fact that, besides being exceptionally interesting materials for basic research programs, they show great potential for many different applications including electrochemistry [8−10], separation science [11−14], chemical synthesis [2, 4, 5, 15−19], and catalysis [4, 5, 17]. Salts with a melting point at or below 100 °C are broadly accepted to qualify as an ionic liquid. However, for many of the above mentioned applications, it is much more desirable to find and develop so called room-temperature ionic liquids. These liquids possess the distinctive characteristics of negligible volatility and consequently no vapor toxicity, great thermal stability, and large liquid range. The ongoing chase after new room temperature ionic liquids with specific chemical and physical properties makes it crucial to incorporate different functional groups. The N-allyl functionality was subject to multiple studies and has been found to effectively suppress crystallization [20−26]. A series of substituted allylimidazolium halides has been obtained as room temperature ionic liquids and some have already been found to be useful as solvents for specific applications [27, 28]. It should be mentioned that methylimidazolium salts possessing alkene- (i.e. allyl-) and alkyne- (i.e. 2-butyne) functionalities have been reported as early as 1971 by *Jones* et al. At that time, they had not been termed ionic liquids. Furthermore, no details on their structural and thermal properties were provided due to the extremely hygroscopic properties of the salts, which made further purification of the compounds more difficult [20]. This paucity of details motivated *Mizumo* et al. to carefully investigate the physical properties of allylimidazolium halides [23]. All salts were obtained as liquids at ambient temperature. However, after storing at low temperature they started to slowly crystallize. In the case of 1-allyl-3-methyl-imidazolium bromide a melting point of +53.1 °C was established which clearly disqualifies it as a true room temperature ionic liquid. Others have reported the same compound having a melting point of −52.5 °C without mentioning a solid state. Today, the compound is commercially available as a liquid (~97 % purity) [24]. These findings provoked us to look further into detailed physical properties of ionic liquids with unsaturated side chains. In the present work, the synthesis of a series of substituted methylimidazolium bromide salts with allyl- **1**, 3-butene- **2**, propargyl- **3**, 2-butyne- **4**, and 2-pentyne- **5** side chains and their structural and physical properties have been investigated. Three of the salts, **1**, **3**, and **4**, have been additionally characterized by single crystal X-ray investigation and exhibit substantial cation-anion interactions via hydrogen bonding.

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Experimental Section

All starting materials were purchased from Aldrich Chemical Company, Inc. and their purities were checked by ^{1}H and ^{13}C NMR

spectroscopy prior to use. The alkyl bromides (allyl bromide, propargyl bromide, 2-butyne bromide, 3-butene bromide and 2-pentyne bromide), methanol (99.93 % A.C.S. HPLC grade) and diethyl ether (anhydrous, 99+%, A.C.S. Reagent) were used as received. 1-methylimidazole was distilled and stored inside a sealed Schlenk vessel under nitrogen. Nonvolatile solids were handled in the dry nitrogen atmosphere of a glove box. Infrared spectra were recorded on a Nicolet 710 SX FT-IR spectrometer from 4000-400 cm^{-1} using dry powders pressed as KBr pellets in an Econo press (Barnes Engineering Co.). Raman spectra were recorded in the range 3500-80 cm^{-1} on a Bruker Equinox 55 FT-RA 106/S spectrometer using a Nd-Yag laser at 1064 nm. Pyrex melting point capillaries or 5 mm glass NMR tubes were used as sample containers. Nuclear magnetic resonance spectra were recorded on a Bruker Spectrospin DRX 400 MHz Ultrashield™ spectrometer at room temperature in DMSO-d_6 solution using 5mm NMR tubes. The ^1H, ^{13}C, spectra were referenced to external samples of neat TMS. Melting points were determined by differential scanning calorimetry using a Thermal Analyst 200, Dupont 910 Differential Scanning Calorimeter. Measurements were carried out at a heating rate of 10 °C/min in sealed aluminum pans with a nitrogen flow rate of 20 mL/min. The reference sample was an empty Al container which was sealed in the nitrogen atmosphere of a glove box. Elemental analyses were carried out on a PerkinElmer 2400 Series II CHNS/Oinstrument equipped with an AD6 Autobalance.

Synthesis of 1-allyl-3-methylimidazolium bromide (1)

1-methylimidazole (4.90 g, 59.68 mmol) was added to a nitrogen-purged, pre-weighed 250 mL Schlenk flask, dissolved in ca. 40 mL methanol and stirred vigorously with a Teflon® stir bar. Allylbromide (14.30 g, 118.20 mmol) was added drop-wise to the continuously stirred solution. The mixture was stirred at 25 °C for several days until TLC (**T**hin **L**ayer **C**hromatography) monitoring indicated a complete reaction of 1-methylimidazole. All volatile material was removed in a dynamic vacuum (15 mbar) at elevated temperature, leaving behind a highly viscous liquid. Great care was taken drying the product and removing traces of solvent. This procedure required up to eight days of pumping in a dynamic vacuum (15 mbar) at temperatures as high as 110 °C and regular rolling of the flask. The purity of the product was frequently checked by ^1H NMR. Only upon storage in a refrigerator, by mechanical stimuli, or after long periods of standing did the liquid finally solidify. However, it could not simply be recrystallized from methanol solutions layered with diethylether. (yield 97 %), mp. 60 °C, DSC decomposition onset 253 °C. $C_7H_{11}N_2Br$: Calc. C, 41.40; H, 5.46; N, 13.79; Found: C, 41.35; H, 5.68; N, 13.58 %.

IR (KBr, cm^{-1}) ν = 3079(s, br), 2942(m, sh), 2856(m), 2058(w), 1646(4), 1573(vs), 1448(s), 1424(s), 1384(w), 1336(m), 1292(w), 1165(vs), 998(s), 947(s), 841(m), 764(s), 675(m), 626(s); **Raman** (500 mW, 25 °C, cm^{-1}) ν = 3077(44), 3011(76), 2978(73), 2945(100), 2883(29), 2824(17), 1645(53), 1562(9), 1413(49), 1384(12), 1331(19), 1292(25), 1222(3), 1164(1), 1094(7), 1021(46), 951(3), 918(3), 761(5), 673(8), 622(12), 569(5), 500(4), 396(7), 357(3), 269(3), 232(4), 112(56), 84(97); δ_H (400 MHz, neat liquid) 8.97 (1H s, br), 7.30 (1H, s, br), 7.27 (1H, s, br), 5.20 (1H, s, br, CH_2CHCH_2), 4.45 (2H, s, br, CH_2CHCH_2), 4.33 (2H, s, br, CH_2CHCH_2),3.30(3H, s, br, CH_3); δ_C (100 MHz, neat liquid) 136.8, 132.0, 124.0, 122.4, 120.7, 51.1, 37.3.

Synthesis of 1-(3-butenyl)-3-methylimidazolium bromide (2)

1-methylimidazole (3.98 g, 48.41 mmol) was added to a nitrogen-purged, pre-weighed 250 mL Schlenk flask, dissolved in ca. 40mL methanol and stirred vigorously with a Teflon® stir bar. 4-bromo-1-butene (14.20 g, 105.18 mmol) was added drop-wise to the continuously stirred solution. The mixture was heated to 50 °C for several days. Following the procedure described above the reaction yielded 66 % of a highly pure product. The relatively low yield was due to an incomplete reaction. mp. 44 °C, DSC decomposition onset 292 °C. $C_8H_{13}N_2Br$: Calc. C, 44.26; H, 6.04; N, 12.90; Found: C, 44.32; H, 5.79; N, 12.19 %.

IR (KBr, cm^{-1}) ν = 3082(s, br), 2848(s), 2071(w), 1641(s), 1574(vs), 1439(s), 1380(w), 1368(w), 1339(m), 1289(w), 1218(w), 1172(vs), 1132(m), 997(s), 930(s), 828(m, br), 752(s, br), 700(m), 661(m), 623(s); **Raman** (500 mW, 25 °C, cm^{-1}) ν = 3130(14), 3087(17), 3073(19), 2997(64), 2974(95), 2951(100), 2926(54), 2909(76), 2864(10), 2835(19), 1640(60), 1558(7), 1458(12), 1414(62), 1377(17), 1335(36), 1294(21), 1279(10), 1231(17), 1216(7), 1161(2), 1134(9), 1089(19), 1033(9), 1014(36), 1001(10), 933(4), 890(7), 849(9), 800(1), 700(19), 657(5), 630(3), 599(24), 463(5), 411(16), 319(4), 266(11), 226(7), 152(40), 110(81), 85(98); δ_H (400 MHz, DMSO-d_6) 9.24 (1H s), 7.82 (1H, dd, J 1.7), 7.74 (1H, dd, J 1.7), 5.81-5.70 (1H, m $CH_2CH_2CHCH_2$), 5.08-5.03 (2H, m, $CH_2CH_2CHCH_2$), 4.27 (2H, t, J 6.9 $CH_2CH_2CHCH_2$), 3.86 (3H, s, CH_3), 2.56 (2H, d, J 6.8 $CH_2CH_2CHCH_2$); δ_C (100 MHz, DMSO-d_6) 137.0, 134.1, 124.0, 122.8, 118.8, 48.3, 36.2, 34.0;

Synthesis of 1-propargyl-3-methylimidazolium bromide (3)

1-methylimidazole (3.71 g, 45.14 mmol) was added to a nitrogen-purged, pre-weighed 250 mL Schlenk flask, dissolved in ca. 40 mL methanol and stirred vigorously with a Teflon® stir bar. Propargylbromide (12.00 g, 100.87 mmol) was added drop-wise to the continuously stirred solution. The mixture was stirred at 25 °C for several days. Following the procedure described above, the reaction yielded 73 % of a highly pure product. The relatively low yield was due to an incomplete reaction. mp. 117 °C, DSC decomposition onset 192 °C. $C_7H_9N_2Br$: Calc. C, 41.82; H, 4.51; N, 13.93; Found: C, 41.52; H, 4.60; N, 13.46 %.

IR (KBr, cm^{-1}) ν = 3175(m), 3130(vw), 3100(vw), 3073(m), 3061(m), 3041(m), 3025(m), 3008(vw), 2952(w), 2934(w), 2906(w), 2848(vw), 2466(m), 2408(m), 2119(s), 1624(w), 1576(s), 1560(s), 1461(w), 1449(w), 1424(m), 1389(w), 1361(w), 1328(w), 1295(m), 1215(w), 1201(w), 1175(vs), 1110(w), 1097(w), 1020(m), 943(s), 866(s), 857(s), 784(m), 754(s), 719(m), 670(m), 622(s), 613(m); **Raman** (400 mW, 25 °C, cm^{-1}) ν = 3163(9), 3129(3), 3102(4), 3073(10), 3063(10), 3027(10), 3009(12), 2985(19), 2955(34), 2930(48), 2908(31), 2860(13), 2820(6), 2117(100), 1560(4), 1476(4), 1460(3), 1448(5), 1408(33), 1388(11), 1348(6), 1328(9), 1294(6), 1215(7), 1202(10), 1174(4), 1116(9), 1097(2), 1032(8), 1021(42), 943(6), 884(1), 869(4), 856(2), 784(1), 750(4), 737(12), 717(5), 671(11), 614(15), 453(11), 402(5), 330(10), 321(16), 283(11), 274(12), 230(8), 149(49), 111(16), 85(17); δ_H (400 MHz, DMSO-d_6) 9.46 (1H s), 7.88 (1H, s), 7.87 (1H, s), 5.35 (2H, d, J 2.5 CH_2CCH), 3.91 (3H, s, CH_3), 3.89 (1H, t, J 2.5 CH_2CCH); δ_C (100 MHz, DMSO-d_6) 136.4, 123.9, 122.0, 78.9, 76.0, 38.6, 36.1.

Synthesis of 1-(2-butynyl)-3-methylimidazolium bromide (4)

1-methylimidazole (4.31 g, 52.54 mmol) was added to a nitrogen-purged, pre-weighed 250 mL Schlenk flask, dissolved in ca. 40 mL methanol and stirred vigorously with a Teflon® stir bar. The mixture was cooled in an ice bath. 1-bromo-2-butyne (9.80 g, 73.69 mmol) was added drop-wise at 0 °C to the continuously stirred solution. The reaction mixture was allowed to warm to ambient temperature and stirred for several days. Following the procedure described above, the reaction yielded 93 % of a highly pure product. mp. 131 °C, DSC decomposition onset 254 °C. $C_8H_{11}N_2Br$: Calc. C, 44.67; H, 5.12; N, 13.03; Found: C, 43.48; H, 5.11; N, 12.95 %.

IR (KBr, cm^{-1}) ν = 3172(vw), 3130(vw), 3096(m), 3004(m, br), 2930(m), 2317(w), 2300(w), 2234(m), 1617(m), 1570(s), 1441(w), 1419(w), 1384(w),

1343(m), 1219(w), 1172(s), 1142(s), 1091(w), 1021(vw), 967(w), 879(m), 787(vw), 758(m), 748(m), 646(s), 623(s); **Raman** (500 mW, 25 °C, cm^{-1}) ν = 3157(5), 3129(7), 3087(16), 2994(20), 2951(70), 2929(69), 2915(100), 2852(21), 2753(5), 2726(3), 2321(11), 2303(7), 2240(48), 1560(6), 1443(15), 1411(41), 1385(23), 1333(14), 1282(8), 1218(8), 1160(2), 1143(1), 1100(5), 1090(17), 1021(9), 1011(13), 965(2), 895(4), 866(1), 797(3), 749(2), 737(10), 716(1), 664(14), 650(3), 619(15), 448(16), 407(13), 361(20), 324(7), 283(2), 246(6), 182(9), 85(98); δ_H (400 MHz, DMSO-d_6) 9.46 (1H s), 7.86 (1H, dd, J 1.7), 7.85 (1H, dd, J 1.7), 5.22 (2H, d J 2.4 CH_2CCCH_3), 3.91 (3H, s, CH_3), 1.863 (3H, t, J 2.4 CH_2CCCH_3); δ_C (100 MHz, DMSO-d_6) 136.8, 124.4, 122.5, 84.9, 72.0, 39.5, 36.5, 3.8;

Synthesis of 1-(2-pentynyl)-3-methylimidazolium bromide (5)

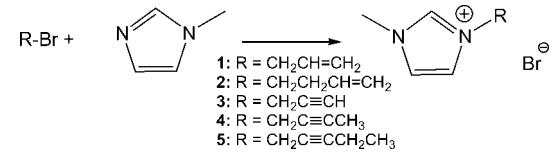
1-methylimidazole (4.02 g, 48.89 mmol) was added to a nitrogen-purged, pre-weighed 250mL Schlenk flask, dissolved in ca. 40 mL methanol and stirred vigorously with a Teflon® stir bar. The mixture was cooled in an ice bath. 1-bromo-2-pentyne (10.00 g, 68.02 mmol) was added drop-wise at 0 °C to the continuously stirred solution. The reaction mixture was allowed to warm to ambient temperature and stirred for several days. Following the procedure described above, the reaction yielded 95 % of a highly pure product. mp. 66 °C, DSC decomposition onset 216 °C. $C_9H_{13}N_2Br$: Calc. C, 47.18; H, 5.72; N, 12.23; Found: C, 46.54; H, 5.65; N, 12.23 %.

IR (KBr, cm^{-1}) ν = 3134(w), 3089(w), 2984(m), 2938(m), 2923(m), 2902(w), 2881(w), 2852(vw), 2458(vw), 2405(m), 2308(m), 2242(s), 2075(m), 2056(m), 1626(s), 1570(vs), 1452(s), 1417(s), 1381(m), 1339(s), 1319(m), 1276(w), 1247(vw), 1211(vw), 1168(vs), 1142(s), 1109(m), 1095(m), 1083(m), 1063(m), 1022(m), 962(w), 869(m), 855(m), 833(m), 781(s), 758(vs), 745(s), 650(s), 625(s), 617(s); **Raman** (500 mW, 25 °C, cm^{-1}) ν = 3141(12), 3124(13), 3098(20), 2976(38), 2938(71), 2921(89), 2910(100), 2851(32), 2784(1), 2723(7), 2631(1), 2579(0+), 2457(0+), 2393(0+), 2303(13), 2281(11), 2232(59), 2199(4), 1558(4), 1447(19), 1429(24), 1417(39), 1377(18), 1333(16), 1276(11), 1229(3), 1213(11), 1160(1), 1137(0+), 1096(9), 1084(10), 1063(7), 1028(11), 1012(40), 960(7), 894(4), 864(1), 827(1), 780(3), 756(4), 730(3), 648(7), 614(11), 520(2), 505(2), 409(18), 329(1), 290(10), 277(11), 217(4), 184(5), 85(81); δ_H (400 MHz, DMSO-d_6) 9.45 (1H s), 7.84 (1H, s), 7.84 (1H, s), 5.25 (2H, s $CH_2CCCH_2CH_3$), 3.91 (3H, s, CH_3), 2.21(2H, q J 7.6 $CH_2CCCH_2CH_3$) 0.99 (3H, t, J 7.6 $CH_2CCCH_2CH_3$); δ_C (100 MHz, DMSO-d_6) 136.6, 124.2, 122.3, 90.3, 71.9, 39.4, 36.5, 13.7, 12.2;

All preparations can be carried out using toluene instead of methanol as a solvent. Products are formed almost instantaneously and crash out of the toluene solution. However, workup proved rather difficult because of the relatively high boiling point of toluene. In some cases, even after multiple washings, the solvent could never be removed completely.

X-ray Analyses

The single crystal X-ray diffraction data were collected on a Bruker 3-circle platform diffractometer equipped with a SMART CCD (charge coupled device) detector with the χ-axis fixed at 54.74°and using MoK_α radiation (λ = 0.71073 Å) from a fine-focus tube. The diffractometer was equipped with a KryoFlex apparatus for low temperature data collection using controlled liquid nitrogen boil off. The goniometer head, equipped with a nylon Cryoloop with a magnetic base, was used to mount the crystals using PFPE (perfluoropolyether) oil. Cell constants were determined from 90 ten-second frames. A complete hemisphere of data was scanned on omega (0.3°) with a run time of ten-second per frame at a detector resolution of 512 x 512 pixels using the SMART software [29, 30]. A total of 1271 frames were collected in three sets and final sets of 50 frames, identical to the first 50 frames, were also collected to determine any crystal decay. The frames were then processed on a PC running on Windows NT software by using the SAINT software [31, 32] to give the hkl file corrected for Lp/decay. The absorption correction was performed using the SADABS [33] program. The structures were solved by the direct method using the SHELX-90 [34] program and refined by the least squares method on F^2, SHELXL-97 [35] incorporated in SHELXTL Suite 5.10 for Windows NT [36, 37]. All non-hydrogen atoms were refined anisotropically. For the anisotropic displacement parameters, the U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor. The hydrogen atoms were located either from difference electron density maps or generated at calculated positions.



Scheme 1 Synthesis of compounds **1** − **5**

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre (CCDC 643670, CCDC 643671 and CCDC 643672). Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code +(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk).

Results and Discussion

Among a series of methylimidazolium halides with unsaturated side chains, 1-allyl-, and 1-propargyl-3-methylimidazolium halides (X = Cl, Br, I), and 1-(2-butyne)-3-methylimidazolium bromide have been mentioned earlier [20, 21, 23−28, 38, 39]. However, detailed physical properties on these compounds are either completely missing or, in the case of **1**, the reported properties are not consistent [23, 24]. Hence, we have prepared a sequence of substituted methylimidazolium bromides, including the previously reported and the novel salts 1-(3-butenyl)- and 1-(2-pentynyl)-3-methylimidazolium bromide, and investigated their physical and structural properties for the first time in detail.

Syntheses and physical properties

The syntheses of the alkene and alkyne substituted methylimidazolium bromides followed the procedure by *Jones* et al. [20]. In a typical experiment, the alkyl halide was used in excess and the reaction was run at elevated temperatures, up to 65 °C, in solvents such as toluene or methanol. Initially, all the substituted methylimidazolium bromides were obtained as highly viscous, slightly yellowish to amber liquids. Only after prolonged storage in a refrigerator, by mechanical stimuli, or after long periods of standing did the liquids start to slowly crystallize or completely solidify. **1**, **3**, and **4** crystallized within weeks upon storage at −18 °C. However, solids generated by this process could not simply be recrystallized from saturated polar solvent solutions layered with diethylether. After recrystallization,

Table 1 Thermal data for the different bromide salts.

	Imidazolium Cation	$T_{g(peak)}$ (± 1 °C)	$T_{m(peak)}$ (± 1 °C)	$T_{dec(onset)}$ (± 1 °C)
1	1-allyl-3-methyl-	−51	60	253
2	1-(3-butenyl)-3-methyl-	−57	44	292
3	1-propargyl-3-methyl-	−20	117	192
4	1-(2-butynyl)-3-methyl-	−5	131	254
5	1-(2-pentynyl)-3-methyl-	−18	66	216

the material was obtained again in the liquid state. This is due to the tendency of forming super-cooled liquids rather than crystallizing upon cooling, a behavior very typical of many ionic liquids. All salts are highly hygroscopic and should be handled in the dry nitrogen atmosphere of a glove box. They are soluble in a wide array of polar solvents, e.g. methanol, ethanol, isopropanol, acetonitrile, dimethylsulfoxide, and are insoluble in ethyl acetate, methylene chloride, diethyl ether, and toluene.

Thermal investigations

The melting, glass transition, and thermal decomposition points (decomposition onset) were determined by DSC analysis (Table 1). Due to the tendency to form super-cooled liquids, these compounds can easily be misjudged as true room temperature ionic liquids. Only by investing the time and patience required to allow materials to crystallize and ensure purity, we were able to discover their accurate physical properties. Melting points range from 44 °C for **2** up to 131 °C for **4**, clearly beyond room temperature. The propargyl- (**3**) and 3-butyne- (**4**) salts possess melting points of 117 °C and 131 °C respectively, and therefore do not even technically qualify as ionic liquids, according to the commonly used definition (i.e. a salt with a mp. ≤ 100 °C). Generally, the salts containing alkyne functionalities show higher melting points and lower decomposition onsets than their corresponding alkene counterparts, most likely due to the "rigidity" of the carbon-carbon triple bond. Samples heated to 150 °C on a DSC and then cooled back to −100 °C using LN_2 did not, upon reheating, display the prior established melting point (with the exception of 1-(2-butynyl)-3-methylimidazolium bromide). Instead, all samples showed glass transition points at low temperatures during a second and third cycle (Table 1). Simply allowing the samples to cool from 150 °C back to ambient temperature by themselves was still too fast to induce crystallization; they remained in a supercooled phase.

X-ray Crystallography

Crystals suitable for single crystal X-ray structure determination were obtained for three of the salts, **1**, **3**, and **4** by storing samples of the liquids at −18 °C for several weeks (Table 2). The different substituents have little effect on the bond lengths and angles within the imidazolium cations. The alkene- and alkyne- groups show no abnormalities within the CC single, double, or triple bonds. The overall packing is dominated by attractive Coulomb forces accompanied by substantial hydrogen bonding from imidazolium ring hydrogens and hydrogen atoms from substituent groups to the bromide anion.

Table 2 Crystal and structure refinement data for substituted -imidazolium bromides.

Compound	1-allyl-3-methyl-	1-propargyl-3-methyl-	1-(2-butynyl)-3-methyl-
Formula	$C_7H_{11}N_2Br$	$C_7H_9N_2Br$	$C_8H_{11}N_2Br$
Space group	$P2_1$ monoclinic	P*bca* ortho.	$P2_12_12_1$ ortho.
a (Å)	5.893(1)	12.593(2)	6.951(1)
b (Å)	9.721(2)	11.969(2)	9.317(1)
c (Å)	7.939(2)	21.745(3)	14.088(2)
β (°)	108.997(3)		
V/Å^3	430.1(2)	3277.5(8)	912.4(2)
$\rho_{calc.}$/g cm^{-3}	1.568	1.630	1.566
Z	2	16	4
Formula weight	203.08	201.06	215.09
μ/mm^{-1}	4.709	4.943	4.445
Temperature (K)	100	100	100
λ(MoKα)	0.71073	0.71073	0.71073
Crystal size/mm	0.20x0.15x0.10	0.25x0.20x0.20	0.86x0.40x0.35
Theta range θ/°	2.71 to 28.20	1.87 to 28.29	2.62 to 26.32
Index range	−7≤h≤7, −12≤k≤12, −10≤l≤10	−16≤h≤16, −15≤k≤15, −27≤l≤28	−8≤h≤8, −11≤k≤11, −17≤l≤17
Reflection collected	4861	35673	9413
Independent [R(int)]/	1976 [0.018]	3989 [0.032]	1854 [0.030]
Obs. refl. ([I > 2.0 σ(I)])	1881	3497	1807
F(000)	204	1600	432
GooF	1.015	1.043	1.092
R_1, wR [I > 2σ(I)]	0.0176, 0.0391	0.0223, 0.0515	0.0165, 0.452
R_1, wR_2 (all data)	0.0188, 0.0393	0.0281, 0.0535	0.0171, 0.455
L.diff. peak/hole eÅ^3	0.54 and −0.22	0.58 and −0.24	0.51 and −0.35
Absorption correct.	SADABS	SADABS	SADABS
Data/restraints/param.	1976/1/135	3989/0/253	1854/0/145
Refinement method	Full-matrix least squares on F^2		

$R_1 = \Sigma \| |F_o| - |F_c| | / \Sigma |F_o|$; $R_2 = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2] / \Sigma(w(|F_o|^2)^2)\}^{1/2}$

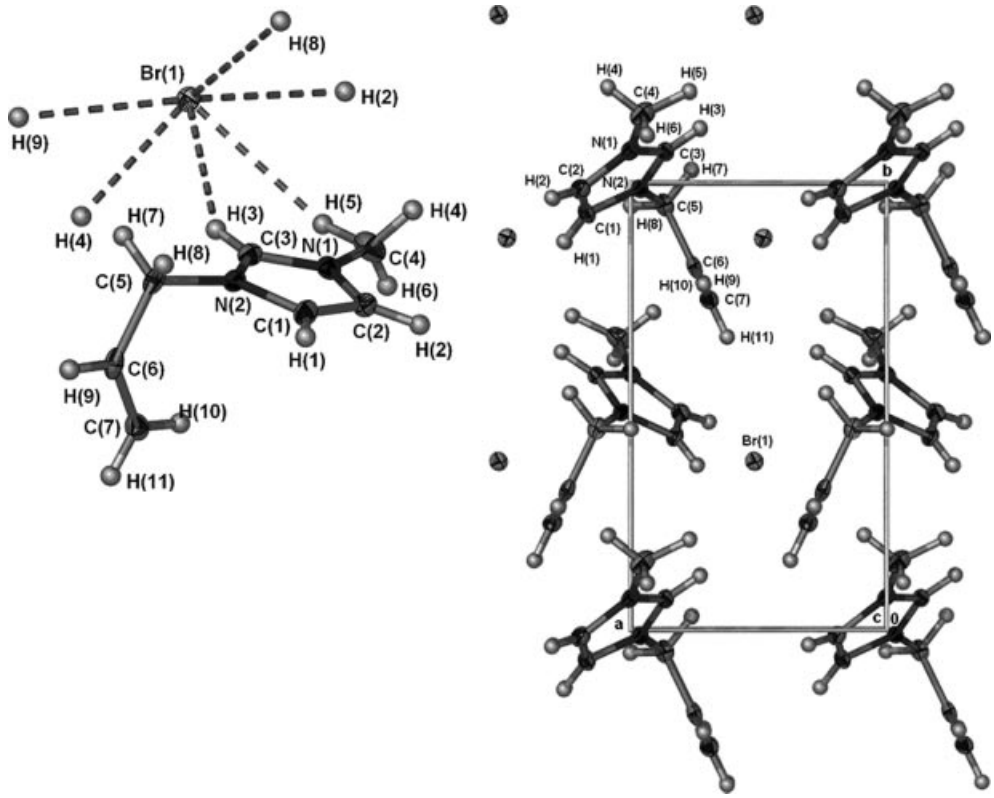


Figure 1 ORTEP diagram showing connectivity, conformation, and the atom numbering scheme of the individual cations and anions present in the asymmetric unit and packing diagram of 1-allyl-3-methylimidazolioum bromide (**1**) along the *c* axis.

1-allyl-3-methylimidazolium bromide crystallized in a monoclinic space group. Figure 1 shows the asymmetric unit and the packing arrangement along the *c* axis. The allyl- chain is oriented perpendicular to the plane of the imidazolium ring and the pendant group arranges like a "C" shaped handle curved towards the imidazolium ring. It exhibits a simple packing with alternating layers of cations and anions. Along the *a* axis, the cations align in offset, zigzag chains. Two intramolecular contacts are present within the cation, i.e. N(2)···H(10) 2.57(3) Å, between the imidazolium ring nitrogen atom N(1) and the terminal allyl proton H(11), which is considerably shorter than Σ_{vdW} (2.75 Å, sum van der Waals radii [40]), and C(1)···C(7) 3.36(1) Å between the imidazolium ring carbon C(3) and the terminal allyl carbon C(7), which is still less than Σ_{vdW} (3.40 Å). These two contacts cause the pendant group to bend towards the ring forming a "C" type handle. The bromide anion shows five strong hydrogen bonds with different cations through the ring, allyl group, and the methyl group hydrogens forming a three dimensional network. They range from 2.76(2) Å, Br(1)···H(3), to 3.00(4) Å, Br(1)···H(5), with the latter being the longest contact just short of the Σ_{vdW} (3.05 Å).

1-propargyl-3-methylimidazolium bromide crystallized in an orthorhombic space group. There are two cation-anion pairs in the asymmetric unit. Figure 2 shows the asymmetric unit and the packing arrangement along the *a* axis. Both asymmetric cations have essentially the same shape and show only small differences in bond length and angles. For both cations, the pendant propargyl groups are again perpendicular to the plane of the imidazloium ring but the straight chain is twisted away from the ring (N(1)-C(4)-C(5) 111.3(1)°, C(3)-N(1)-C(4)-C(5) dihedral twist = 64.7(2)°; and N(3)-C(11)-C(12) = 111.3(1)°, C(10)-N(3)-C(11)-C(12) dihedral twist = 69.3(2)° respectively). There are significant hydrogen bonds, and intermolecular cation-cation contacts present in the crystal structure. The bromide anion is connected to different cations by a total of seven hydrogen bonds forming a three dimensional network. Similar to the case of the allyl substituted salt, the hydrogen atoms of the ring, propargyl group, and the methyl group are participating in the bonding, which range from 2.66(2) Å, Br(2)···H(10), to 3.01(2) Å, Br(1)···H(5). The bromide anion connects with two different cations via a ring proton from one of the cations and either a terminal or central hydrogen of the propargyl group from the other cation (Figure 2). The two asymmetric cations show different connectivity patterns via C(6)···H(9f) 2.73(2) Å, C(6)···C(1) = 3.346 (3) Å, C(13)···H(11o) 2.74(2) Å and C(13)···C(8q) 3.349(2) Å respectively. Only one contact connects the two different cations with each other, C(6)···C(8q) = 3.278 (3) Å. The cations and anions pack by forming alternating layers. However, the two asymmetric cations show very different motives in their packing assembly. One layer consists

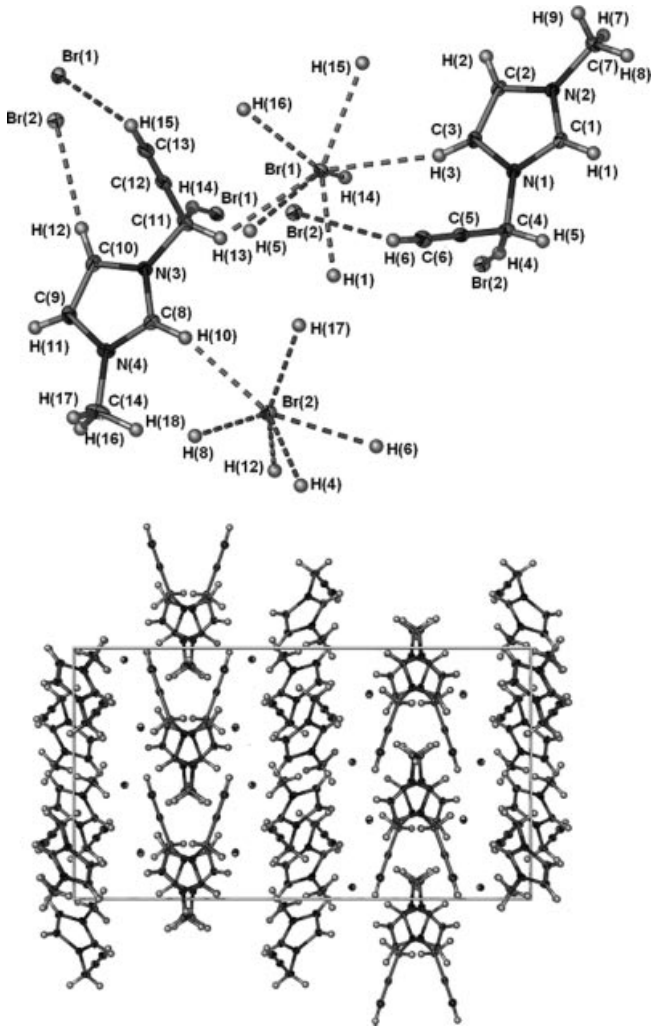


Figure 2 ORTEP diagram showing connectivity, conformation, and the atom numbering scheme of the individual cations and anions present in the asymmetric unit and packing diagram of 1-propargyl-3-methylimidazolioum bromide (**3**) along the *a* axis.

of one of the cations which pile on top of each other along the *a* axis forming a "V" shape structure with the pendant propargyl groups and the "V" shapes stacking along the *b* axis (Figure 2). In the other cation layer, the propargyl groups orient almost parallel to each other which results in a much less structured arrangement.

1-(2-butynyl)-3-methylimidazolium bromide crystallized in an orthorhombic space group. Figure 3 shows the asymmetric unit and the packing arrangement along the *a* axis. The 2-butynyl group is perpendicular to the plane of the imidazolium ring consistent with the previous examples. Like the propargyl- group, the linear butynyl- pendant chain is twisted in the same way, away from the ring by 111.0(2)° (N(1)-C(4)-C(5)). The dihedral twist, however, is considerably smaller with only 7.3(2)°. The bromide anion shows again extensive hydrogen bonding ranging from a strong Br(1)···H(1) bond with 2.69(2) Å to an extremely weak Br(1)···H(11) bond of 3.05(2) Å, which matches the Σ_{vdW} (3.05 Å) (Figure 3). Other contacts include an intermolecular cation link between C(1)···C(7a), 3.384(3) Å, and a strong intramolecular connection between C(5)···H(1) 2.59(2) Å, which is significantly shorter than Σ_{vdW} (2.90 Å). Via this intramolecular contact H(1)-C(1)-N(1)-C(4)-C(5) form a five membered ring structure which prefers a planar configuration explaining the small dihedral twist.

Conclusion

In this work, the focus has been on the structural and physical properties of a series of previously and newly prepared alkene- and alkyne- substituted methylimidazolium bromide salts. The true nature of these ionic liquids can be easily overlooked because of their tendency to form supercooled liquids rather than to crystallize. The results from this investigation should raise some caution in future work to identify room temperature ionic liquid. All salts, obtained as liquids at first, possess melting points significantly

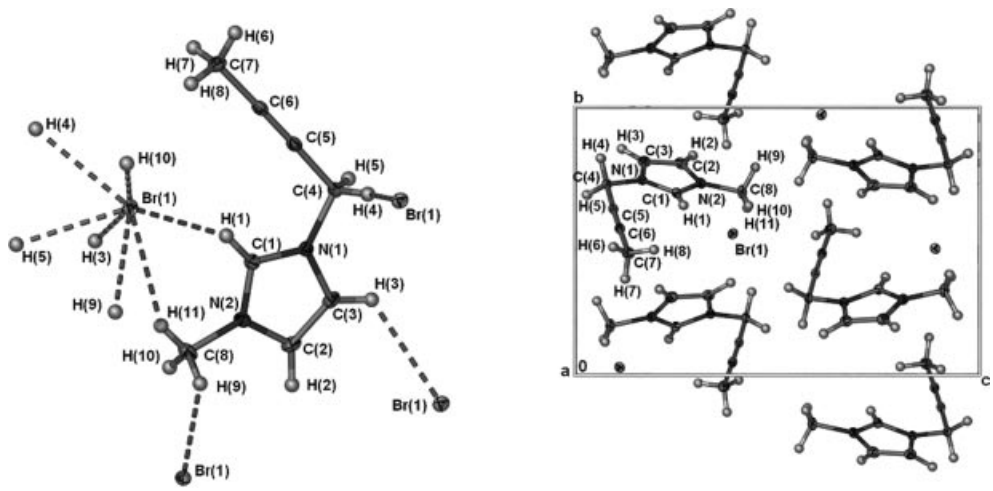


Figure 3 ORTEP diagram showing connectivity, conformation, and the atom numbering scheme of the individual cations and anions present in the asymmetric unit and packing diagram of 1-(2-butynyl)-3-methylimidazolioum bromide (**4**) along the *a* axis.

above room temperature and two of the salts, **3** and **4**, do not even technically qualify as ionic liquids. The three crystal structures showed that hydrogen bonding is extremely dominant in the solid state of these bromide salts which explains the relatively high melting points.

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